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REVIEW OF OXIDATIVE DEGRADATIONS OF CERTAIN HETEROCYCLIC POLYMERS

By Frank R. Mayo

November 1971

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ABSTRACT

The curing and decompositions of polyphenylenes and several nitrogen containing condensation polymers, particularly polybenzimidazoles and pyrrones, are reviewed critically. It is concluded that the condensations are usually imperfect and incomplete and that in most of the published work the late stages of the condensation are complicated by the beginnings of the charring and carbonization processes. Most discussions of mechanisms in this range are highly speculative and of little value. The most promising fields for further research are at lower temperatures, where slow oxidation processes deserve study, and at higher temperatures, where it may be possible to influence carbonization processes to obtain better products.

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INTRODUCTION

The object of this report is to review some of the literature on the degradation of conjugated aromatic and heterocyclic polymers, to deduce the most probable mechanisms of degradation, and to indicate what kinds of experiments should be most useful in testing these mechanisms and in preparing polymers at lower cost or with improved aging characteristics.

To distinguish between the data and conclusions of the authors I cite and my own deductions, conclusions, and opinions, I shall enclose my own in brackets, [ ]. Except for a few temperatures in ^{o}K, all temperatures are in ^{o}C.

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SUMMARY

The section on Background shows that there are two major kinds of service ranges for high-temperature polymers, about 300°, and much higher. The degradation mechanisms and techniques for examining them differ. Pyrolyses of the 300° service polymers, with fairly definite structures, eventually lead to residues approaching graphite and polymers of the second group, with hopelessly complicated and irregular detailed structures.

The preparations, curing, and pyrolyses of polyphenylenes and poly (chlorophenylenes) are discussed. Methane is one of the pyrolysis products of the former polymer. Decompositions of polyphenylene into graphite and methane, or into graphite and hydrogen, are exothermic at all temperatures, but the first is favored thermodynamically up to 550°C, the second above that temperature. The mechanism probably involves contributions from free radical reactions, acetylene and benzyne intermediates, and reorganizations of benzene nuclei. The latter are required by the formation of methane, the loss of heteroatoms, and the formation of graphitic structures; they may occur heterogeneously on surfaces intermediate between polynuclear hydrocarbons and graphite. Poly(chlorophenylenes) have been made from both chlorobenzenes and chlorination of polyphenyls. Although they cure and pyrolyze differently, the end residues are probably the same.

The preparations and pyrolyses of the polybenzimidazoles and then of the pyrrones are then taken up. Few of the available experiments deal with the early onset of decomposition or with the carbonization process; most of them are concerned with short-time experiments in the intermediate temperature range where conventional organic reactions are phasing out and carbonization is setting in, an unsatisfactory region for studying

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either mechanism. There are repeated indications that condensations are imperfect and incomplete, particularly in large-scale reactions, and that pyrolysis accompanies the later stages of condensation. I found no evidence that any of the polymers are stable indefinitely at 300° in air, but all give 70% to 80% yields of char when heated in vacuum. Perhaps the most intriguing observation with one pyrrone film is that its oxidation is strongly autocatalytic after an induction period at 450°. The performance of the chars in ablation shields seems to depend more on their densities (porosities) than on the polymers from which they were made.

The work of Gaudiana and Conley on polybenzimidazole and pyrrone models is reviewed. Since the models could be recrystallized and sublimed, their "purities" are considerably higher than those of any available polymers. The models seem to be slightly more stable than the polymers, but otherwise they seem to be useful models. The models start to decompose in air near 300°, but unfortunately most of the experiments were carried out at higher temperatures or for too short times to bring out differences among polymers or the initial steps in their degradations.

The pyrolyses of aromatic polyamides and polyimides are reviewed briefly. They are less stable than the polybenzimidazoles and pyrrones. Large and relatively easy losses of carbon dioxide on vacuum pyrolysis may provide clues to decomposition of other heterocyclic polymers.

My most useful findings on the decompositions of all the polymers and models above are summarized in the section on "Conclusions." The last section of this report lists numerous suggestions for further work.

BACKGROUND

[There appear to be two major groups of outlets for aromatic and heterocyclic polymers for high-temperature service. The first group includes the polymers that must maintain their initial dimensions, tensile strength, flexibility, impact resistance, and color during service. The upper limit of service for most such polymers at 300° in air, 400° to 500° in vacuum. The second group includes the polymers that can undergo moderate changes in dimensions and physical properties after a cure during which much of the total change takes place. Such polymers are used in ablation shields and brake shoes. They can last indefinitely at 1000° in the absence of oxidizing agents, but their precursors gradually oxidize above 300° in air. In general, most polymers of the first group become polymers of the second group on heating, and all ultimately approach graphite in their properties on sufficient heating in the absence of oxygen. However, real graphitization requires temperatures above 1000°. The chars formed at lower temperatures are probably closer to carbon black than to graphite, except for their states of subdivision.]

[The problems of mechanisms of degradation then fall into two groups: (1) What are the initial stages of decomposition of Group 1 polymers that are responsible for loss of their most important physical properties? This problem is complicated when the condensation is incomplete and when unreacted or different functional groups provide sites for initiation of degradations. (2) What can we say or do about the reoganization of aromatic or heterocyclic nuclei into carbonized products at high temperatures that will improve yields or properties of the chars? With increasing temperature, there is probably a steady evolution of the first type of mechanism into the second. The transition

is probably the most complicated and least rewarding region to study; here the advanced stages of a conventional pyrolysis are hopelessly mixed with incipient carbonization.]

Workers in the field have discussed mechanisms almost entirely in terms of free radicals. [My own opinion is that the mechanisms are probably hopelessly complex and that some nonradical mechanisms deserve consideration.] Fields and Meyerson[1*] have investigated the gas-phase pyrolysis of numerous aromatic compounds at around 700° and have concluded that benzyne is often a significant intermediate. Benzyne participation is best established in the pyrolyses of o-anhydrides (with loss of CO and CO_2) but is also indicated in pyrolyses of chlorbenzene and bromobenzene. Phthalic anhydride and acetylene, a common pyrolysis product, often give similar pyrolysis products, perhaps because acetylene and diacetylene can give benzyne reversibly. [The heterocyclic polymers made from o-dibasic acids should also be capable of giving benzynes.]

At a recent IUPAC Conference, A. A. Berlin[2] summarized his many years of work on conjugated aromatic polymers. Because these views overlap my own and provide a frame of reference for this report, they are summarized here and the full reprint is attached as an appendix.

When a conjugated aromatic polymer is heated at (say) 300° in the absence of oxygen, a small fraction of its weight is lost rather rapidly but weight loss then ceases. When the temperature is increased to 350°, there is again an initial weight loss and again a steady weight. The same sequence appears at 400°, and so on. During these heatings the residues gradually lose their characteristic IR absorption bands, increase in carbon content, aromatic structure, ers absorption, softening point, and depth of color, and become less soluble.

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* References are listed at the end of the report.

Belova and Berlin[2] interpret these results as follows. On the initial heating, free radicals are formed by thermal cracking of the weakest bonds, and some heteroatoms may be eliminated. The resulting radicals give crosslinking by reaction with each other or addition to conjugated systems. At a single temperature these processes continue until development of further conjugation is prevented by structual factors or restriction of coplanarity. At higher temperatures, further development of conjugation becomes possible. The final result is a graphite-like structure. Belova and Berlin[2] consider that although the conjugated aromatic polymers as a class differ in details of structure, molecular weight, and extent of conjugation, their thermal stabilities are due to their common ability to be transformed by heating into more stable, still more aromatic, and crosslinked structures. This process can be considered to be a degradative polymerization. It contrasts with the pyrolysis of unconjugated polymers (e.g., polystyrene), where degradation into small and volatile units continues to high conversions. Thus, the many different conjugated aromatic polymers have somewhat different initial stabilities (because reactions start at different points) but nearly identical properties and stabilities after heating to 800° in vacuum. The heteroatoms may affect the initial molecular weights, softening points, crystallinities, and pyrolyses, but they have little effect on the ultimate graphite-like structure (which may still contain heteroatoms).

Heating a conjugated aromatic polymer in air does not lead to a steady weight (as in vacuum) but usually to an autocatalytic loss of weight and ultimate disappearance of the polymer. Thus, when poly(phenylacetylene) is heated in air at 400°, there is a fast initial weight loss and a tendency toward a steady weight, but then a fast autocatalytic oxidation sets in. The weight loss data suggest that the first weight

loss is the same in air and in vacuum. Although "polynaphtholylene-bis-benzimidazole" loses only 20% of its weight on heating in vacuum to 800°, it is completely volatilized on heating to 630° in air. The weight loss in air is increased by preheating the polymer to 350° in vacuum. Although this preheating causes no noticeable change in elementary composition, it causes a decrease in solubility of the polymer in sulfuric acid. These processes apparently lead to strains and defects that accelerate oxidation. There are only occasional references to this important point in the rest of the literature that I shall cite.

PREPARATIONS AND PYROLYSES OF POLYPHENYLENES

Noren and Stille[3] have just published a review of "methods of synthesis, physical properties, and uses of high-molecular-weight polyphenylenes." The treatment of degradation is rather brief, and the authors point out the difficulty of comparing the products and results of different authors because of the lack of standard tests. Much of the review deals with phenylated and fluorinated polyphenylenes.

Material Balance on Pyrolysis of Polyphenylene

The report of Vincent and Hamermesh[4] is concerned with the syntheses and pyrolyses of polyphenylenes and chlorinated polyphenylenes. Of most interest to me are their data on products of pyrolysis in helium at 900° of their purest p-polyphenylene, containing 0.8% of chlorine. This report states that this pyrolysis gave 14 to 15% of (hydrogen + methane) [but since the starting material contained only 5.2% hydrogen, large amounts of methane must have been formed. I therefore calculated the elementary material balance shown in Table I.]

[There are two limiting cases: (1) If the residue ("char") is 100% carbon, then by carbon balance 86% by weight, 45 mole%, of the (hydrogen + methane) is methane; (2) if the (hydrogen + methane) is 100% methane, then by hydrogen balance the residue contains 1.2% hydrogen. The average of the limiting cases is 72 mole% of methane in the (hydrogen + methane).]

Table I

MATERIAL BALANCE ON PYROLYSIS OF 100 g POLYPHENYLENE AT 900°C

	Product (g)	Carbon (g)	Hydrogen (g)	Chlorine (g)
Starting material	100.0	94.0	5.2	0.8
Pyrolysis products				
Benzene	4.1	3.78	0.32	
Biphenyl	2.5	2.34	0.16	
Terphenyl	1.4	1.31	0.09	
Quaterphenyl	0.8	0.75	0.05	
Hydrogen	14.6 [a]		2.04[b,c] (0[d])	
Methane		10.02[b,c] (10.92[d])	2.52[b,c] (3.66[d])	
HCl	0.8		0.02	0.8
Residue	75.8[a]	75.8[b] (74.9[c,d])	0.00[b] (0.90[c,d])	0.0[b]

[a] Stated yields of 14 to 15% (H_2+MeH) and 75 to 76% char are adjusted in the table to account for 100% of starting material.
[b] Assuming residue to be pure carbon.
[c] By difference.
[d] Assuming that (H_2+MeH) is 100% MeH.

Implications of Material Balance

[These results, in conjunction with Ref. 2, suggest that there are two limiting routes for the pyrolysis of polyphenylene,

$$(-C_6H_4-)_n \rightarrow 6nC + 2nH_2 \quad (1)$$

$$(-C_6H_4-)_n \rightarrow 5nC + nCH_4 \quad (2)$$

and that the second may be the more important one. At my request, Dr. David M. Golden has calculated the free energy changes for these two reactions at four temperatures, as shown in Table II. These results show that p-polyphenylene is unstable with respect to both sets of decomposition

Table II

FREE ENERGY CHANGES (ΔG°) FOR REACTIONS 1 AND 2
(kcal/mole per $-C_2H_4-$ unit at 1 atm)

	298°K	700°K	1000°K	1200°K
Reaction 1	-36.3	-84.1	-136.4	-176.1
Reaction 2	-48.5	-87.1	-121.8	-166.2

products, but particularly at higher temperatures. The more stable decomposition products at room temperature are graphite and methane, but above about 820° K (550°C) carbon and hydrogen become the more stable products. While the other numbers in Table II depend upon several assumptions, this change-over point does not. These results suggest that up to one-sixth of the carbon in polyphenylene may be lost as methane on pyrolysis, with greater shrinkage than if hydrogen were the major gaseous product, and that the pyrolysis temperature and added catalysts might affect the competition between reactions (1) and (2). However, a different mixture of experiments in a later paper by the same author,[5] but apparently based on the same research contract, throws doubt on the high yields of methane. This paper cites an 82% char yield and says that the hydrogen-methane mixture formed by pyrolysis of polymer on a hot nichrome coil was 95% hydrogen. The detailed reports to resolve these questions are not readily available.]

Mechanisms of Pyrolysis

The mechanism of the pyrolysis of polyphenylene (Ref. 4, page 6) is discussed in terms of dehydrogenation; [this must occur but the data suggest that demethanation could also be important in the pyrolysis described. I now modify the authors' mechanism[4] in the light of Ref. 2. The formation of methane shows that the pyrolysis is more complex than the coupling of phenyl rings by dehydrogenation. There must also be considerable

disproportionation of C-H bonds among adjacent nuclei; formation of methane must be balanced by formation of fused rings with more and less than six members. Some of these rings must be strained and reactive (e.g., toward oxygen) until they can reorganize to approach a graphite structure. The thermodynamics of these changes are highly favorable to reaction, but the activation energies are high. The reactions are occurring in a medium resembling the surfaces of carbon black particles. It may be possible to catalyze either or both reactions, and even to retard the graphitization.]

In more recent work on poly(1,4-phenylene), Ehlers and cowarkers[7] heated this polymer in vacuum to 450°, 500°, and 620° until gas evolution practially ceased at each temperature. Then the residues, readily volatile materials, and high-boiling products were weighed, and the first two of these were analyzed. The initial polymer was made from benzene and ferric chloride and contained 6.2% Cl, 1.2% 0, and 1.6% ash. At 450° essentially all of the oxygen and chlorine were lost, the latter partly as HCl but mostly as unidentified compounds, and the residue averaged $C_6H_{3.4}$. The oxygen was lost as water, CO_2, and CO in that order of importance. The total weight loss up to 620° was 20.7%, about half as high-boiling products (polyphenylenes), and the final residue averaged $C_6H_{1.4}$. The gases other than those specified above were mostly hydrogen and methane.

Lancaster and Wright[8] have compared the rates of weight loss of m-polyphenylene in air and in vacuum. For a 25% weight loss in 2 hours, 440° is required in vacuum, only 324° in air.

[The work above suggests three additions to my conclusions on the work of Vincent et al.[4] (1) It supports Berlin's idea that additional reactions occur at increasing temperatures and that the products approach graphite. (2) The Ehlers work gives thermogravimetric analyses of polyphenylene in nitrogen and in vacuum. At 900°, 23% of the starting

material was lost in vacuum, only 15% in nitrogen. Apparently, many of the volatile polyphenylenes are removed in vacuum, but are pyrolyzed to add to the residue at atmospheric pressure. (3) The H_2/CH_4 mole ratio is 6 to 16 at various temperatures in the Ehlers work, nearer to the higher Vincent value[5] than to my calculations. I see three possible reasons: (1) the differences between pyrolyses at low and atmospheric pressures, (2) catalysis of hydrogen formation by the 1.6% of ash (probably iron oxide) in the Ehlers polymer, and (3) an error in the Vincent data or my interpretation of them that caused me to count missing carbon as methane.]

Preparations of Chlorinated Polyphenylenes

Vincent and Hamermesh prepared their chlorinated polyphenylenes in two ways.[4] (1) "Post" chlorinations of suspensions of polyphenylene were carried out with $CuCl_2$ as chlorinating agent and $AlCl_3$ as catalyst, or with a combination of chlorine and ferric chloride. [The data indicate that the latter chlorination would be faster and more extensive if it were carried out under higher temperatures and pressures.] Yields of recovered polymers were high. (2) The "direct synthesis" started with refluxing benzene and effected chlorination and condensation simultaneously with a combination of $AlCl_3$ and $CuCl_2$. Yields of 50 to 60% of the desired product containing 4% chlorine were obtained. This low yield represents the polymer that could be precipitated by methanol. Some "suggestions for further work" appear near the end of that section.

Pyrolyses of Chlorinated Polyphenylenes

The two kinds of chlorinated polyethylenes lost weight at different rates at various temperatures but eventually yield essentially the same char. Although the Vincent and Hamermesh report (Ref.4, page 6) discusses

the pyrolysis of chlorinated polyphenylenes in terms of chlorine elimination, [the main reaction must be dehydrochlorination. I expect that loss of hydrogen chloride will be easier than loss of either hydrogen or methane.]

[This difference between the two kinds of chlorinated polyethylenes should be expected. The post-chlorinated products are essentially chlorine-substituted polyphenylenes; they contain close to 4 (H + Cl) atoms per C_6 unit (four is theoretical for an uncomplicated polyphenylene system). Twenty-five percent of the original phenyl-H bonds must have been converted to crosslinks or incorporated in new rings. These products are farther along the way to the final char.]

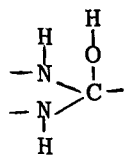
The ablative performances of several polyphenylenes were compared by heating them with an oxyacetylene torch. The best results were obtained from the chlorinated and cured (usually fiber-filled) products. [I take these results to mean that near-graphite is the desired ablative material. The closer the cured polymer is to graphite, with respect to crosslinks and potential volatile material and volume change, the less will be the strains and fissures developed when the article is subjected to sudden and extreme changes in temperatures.]

PREPARATIONS AND PYROLYSES OF POLYBENZIMIDAZOLES

Laboratory Preparations and Pyrolyses

Searches for polymers serviceable at high temperatures have centered on aromatic compounds with condensed rings. Many of the heterocyclic rings contain nitrogen but some contain oxygen or sulfur. Although the presence of oxygen contributes to the instability of the polymers at high temperatures, a carbonyl group is preferable to a methylene group at lower temperatures.

The presence of heterocyclic nitrogen is least harmful, but the presence of nitrogen or oxygen or both is essential for making aromatic high polymers easily from reasonably available starting materials. This section is concerned with the polybenzimidazoles and particularly with the polymer made from diphenyl isophthalate and 3,3'-diaminobenzidine, often designated PBI. Its formula and quantitative considerations in its synthesis are given at the beginning of the next section. When the monomers are heated in vacuum for 30 minutes at 260°, the off-gases contain 92 to 100% of the theoretical phenol (lost first) and 45 to 61% of the theoretical water. Infrared absorption of this polymer suggests the group



but elementary analysis shows that it contains $2H_2O$ above the formula weight of PBI,[9] perhaps partly abosrbed from air at room temperature. When this polymer is pulverized and heated to 400° for 9 hours in vacuum, it attains the correct elementary analysis.

Shulman and Lochte[10] reported the decompositions of similar polymers up to 916° in vacuum with mass spectral analyses of gases and elementary analysis of residues (unsatisfactory at high temperatures). The gases produced depended on pretreatment of the polymer. One sample was prepared by heating for 3 hours at 300° under nitrogen, then for 3 hours at 300° in vacuum, giving a moulding powder which was pressed for 2 hours at 400° under 2000 psi pressure. Filings from this moulding were then heated to 840° at the rate of 20°/min. Water was nearly the sole product up to 530°, the major product up to 630°, and still important at higher temperatures. Ammonia, HCN, and hydrogen appeared in that order at 500° to 530° and became major products at 630° to 730°. The total volatile fraction was 38% water, 30%, HCN, 13% each of H_2 and NH_3, 4% of CO, 1.5% CH_4, 0.9% of phenol (around 600°), and 0.3% CO_2. Since theoretically PBI contains no oxygen, the sustained evolution of water shows that the condensation was incomplete after all the curing. When another sample was aged for one hour at 400° under nitrogen and then (no details) at 520°, H_2, CO, CO_2 were the principal products, in that order, at rates increasing fairly regularly from 600° to 900°. Activation energies are estimated from TGA as 18 kcal/mole for the low-temperature reaction, 34 kcal/mole for the high-temperature reaction, [but I doubt that these have much quantitative significance.]

I now take up the experiments of Conley and coworkers on "purified" PBI supplied by the Materials Laboratory of Wright-Patterson Air Force Base. In one instance,[11] they used the appearance and growth of the infrared-$C \equiv N$ absorption band in cast films of PBI as a measure of decomposition, both in the presence and absence of oxygen. In the absence of oxygen, no $-C \equiv N$ band appears much below 500°, but it appears after about 300 minutes at this temperature. The other PBI bands, although somewhat broadened and weakened, are still distinguishable. Although these bands indicate extensive decomposition of PBI in 150 minutes

at 500°, the -C ≡ N band is still becoming stronger. [These data seem to be as good a measure as we have of the inherent stability of fairly good PBI in the absence of oxygen.]

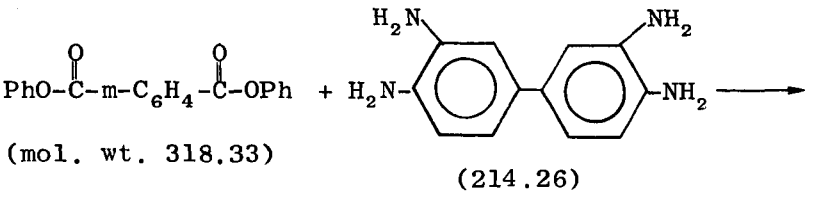
The appearance of the -C≡N band was also used to follow the decomposition of PBI in oxygen streams.[11] This band was detected after 41 hours at 250° but did not appear below this temperature. More -C≡N absorption developed in one hour at 300° than in 100 hours at 250°. During 7 hours at 350°, the -C≡N absorption increased steadily while the characteristic PBI absorptions become indistinguishable. Extensive degradation occurred in 20 minutes in oxygen at 420°. At 500°, the gaseous products are $CO_2 > CO >> (CN)_2$ (probably)[12]; 1,3-dicyanobenzene was identified in the distillate. The same products were obtained at 400°, but at a lower rate. The above experiments show that oxygen markedly decreased the temperature of onset of the initial decomposition of PBI.

The same authors measured[13] the amounts of weight lost when samples of PBI were heated in oxygen streams for 30 minutes at constant temperatures. The weight losses in percent at 250°, 300°, 350°, 400°, and 550° were: 8.7, 8.7, 11.6, 93.7, 95.0 [The IR method did not detect the 8.7% weight loss in 30 minutes at 250°, and one wonders whether this weight loss is water, solvents, or polymer fragments.]

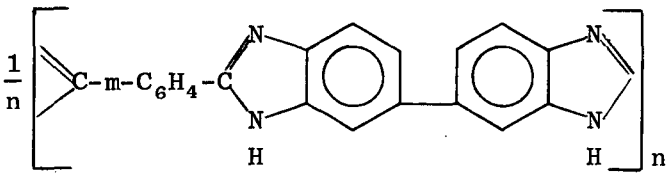
The earlier report[11] states that a sample of PBI film, heated for 3 hours at 450° under helium (where decomposition is first detectable at 500°) oxidizes faster at 300° [has a half-hour head start] than an untreated sample. Preheating at 300° had no effect. Thus, decompositions of PBI that have usually escaped notice can be detected by such sensitive methods.

Practical Preparation and Crosslinking of PBI

PBI is made by the condensation of 3,3'-diaminobenzidine and diphenyl isophthalate:



(mol. wt. 318.33) (214.26)



(308.34) (2x94.11) (2x18.016)

The starting material is a commercial prepolymer where N is said to be 2 to 3. By TGA, "it was found that elimination of end groups (through evolution of phenol and water) was not complete until a temperature of at least 400° was reached, whereupon a stable high-molecular-weight PBI was formed" (Ref. 6, p. 576). These prepolymers were first cured at a temperature of 400° to give "an essentially linear PBI polymer which was free of the easily degraded end groups. Post-curing of these linear polymers, in an inert gas environment at a heating rate of 3°C/min, gave a tough, black solid in yields of about 85%. In the post-cure process, the hydrogen atoms are driven off but the heteroatoms are retained." The result is a "thermally crosslinked" structure with an empirical formula of $C_{47}H_{14}N_8)_n$ (Ref. 6, p. 576). The PBI resin alone is still thermoplastic from 400° to 450° and does not become thermoset until about 480° to 510° (Ref. 14, p. 2-2). Marks et al.[14] are concerned mostly with the fabrication of shaped polymers from a composite of PBI, carbon fiber, and either phenolic or glassy carbon microballons. The commercial starting prepolymer lost 20 to 21% of its weight on heating in air to 260°,

another 9 to 12% on heating in nitrogen to 510° (Ref. 14, p. 3-7). The prepolymers were also examined by thermogravimetric analyses. Prepolymer was first cured by gradual heating from 121° to 316° during 4 hours in nitrogen (Ref. 14, pp. 3-12, and A-6). Then 250-mg samples were heated in helium at the rate of 6°/min. Figures 3 and 4 of Ref. 14 show that 4 to 5% of the sample weights are lost on heating in helium below 200°, then no more until 600° is reached. The total weight loss from the cured polymer at 1000° is 25% by the figures (Ref. 14, p. 3-10), 21.1% by the text.

[When I put these data[6,14] together, I conclude that the prepolymer has less than the supposed degree of polymerization or considerable free phenol or both, and that the PBI starts to decompose ("crosslink") before the condensation is complete. The weight losses on heating the prepolymer are too high for its stated composition. For a prepolymer averaging 2 repeating units, the theoretical weight loss to give high-molecular-weight polymer would be 26.44%; if it averages 3 units, the loss would be 19.5%, but the observed weight loss on heating to 260° and then 510° is 30%.[14] This loss is too large for either n = 2 or 3 in the prepolymer, even if the condensation is complete at 510°, but the following data show the need to establish this extent of completion.]

[Table III compares the empirical formulas and elementary analyses for high-molecular-weight PBI and for the post-cured polymer formed in 85% yield at 800° from supposed linear PRI (cured at 400°, no analysis given).[6] The table shows that if the cured polymer is really theoretical PBI, then 10% of its carbon and 15% of the polymer weight are lost in the post-cure. However, the following observations raise doubts about the true composition of the supposed linear PBI cured at 400°.[4]] Gray et al.[9] found that PBI retained water tightly and that it had to be pulverized and heated in vacuum for 9 hours at 400° before it attained the correct analy-

sis. Marks et al.[14] report that PBI does not become thermoset (I take this to mean high enough molecular weight to become infusible) until about 480° to 510°. [It therefore appears that losses of water and phenol may complicate the results in Table II and that an experimental analysis of the supposed linear PBI is needed. (A PBI heptamer would lose 9.4% of

Table III

CHANGES IN COMPOSITION IN PBI DURING CURING

Empirical Formula →	Theor. for PBI $C_{20}H_{12}N_4$	Post-Cured PBI[a] $C_{20}H_6N_{3.4}$	Loss on Post-Cure[b]
C,%	77.89	81.7	10.7
H,%	3.93	2.1	55
N,%	18.18	16.2	24

[a] Calculated from stated empirical formula, $C_{47}H_{14}N_8$.[6]
[b] Percent of each original element in "linear PBI" lost, calculated for 85% yield of post-cured polymer.

its weight on condensation to a high-molecular-weight polymer, a pentamer, 12.5%). During the post-cure, the C/H ratio in the polymer almost certainly increases, more than can be accounted for by loss of phenol alone. Accordingly, free hydrogen, water, and methane are probably also evolved. If much methane is evolved, there must be considerably more reorganization of aromatic nuclei than the reports suggest.[6,14] In spite of the high carbon losses on post-cure the last column shows that proportionately much more nitrogen than carbon is lost, contrary to the quotation above.]

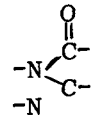
Thermogravimetric analysis of PBI in air show that weight loss begins at 260° and that the polymer disappears without formation of char.[6] [Although the oxidation is attributed to the sensitivity of the N-H groups, I suspect that most hydrogen-containing, uncrosslinked polymers will oxidize similarly without charring.] However, very rapid heating, as in arc-heated air streams, apparently results in a pyrolysis that is faster than the oxidation, perhaps because of formation of a protective coating, and considerable char is obtained.[6]

"Chemical crosslinking" to supplement thermal crosslinking was explored by two routes. In one, 3,3'-diaminobenzidine was oxidized by an unspecified method to introduce "effective functionalities greater than 2. Such structures have a number-average molcular weight about double that of the monomer with a 10% reduction in primary amine contents."[6] [These data appear to mean that coupling of two molecules (with four amine groups each) results in the loss of about 0.8 amine group. Loss of each amine group prevents the other group of the pair from forming a benzimidazole ring and permits formation of an amide.]

The other route to chemical crosslinking replaced part of the diphenyl isophthalate with triphenyl trimesate (1,3,5-benzene-tricarboxylate). Since these products did not perform as well in ablation tests with added carbon fiber and microspheres as the other crosslinked products, "it was concluded that the second type of chemical crosslinking interferes with the formation of a stable cross-link structure at high temperatures".[6] [However, the data presented do not justify this conclusion. There is a good correlation between the rates of weight losses in ablation experiments and the densities (i.e., porosities) of the test materials. The thermally crosslinked material has the highest density (0.55) and the lowest rate of weight loss. The triphenyl trimesate material has the lowest density (0.416) and about twice the rate of weight loss. The oxidized benzidine product has an intermediate

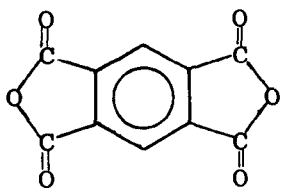
density (0.496) and an intermediate weight loss, closer to the thermal product. When comparisons are made at the same material densities, I suspect that the differences will approximate the experimental errors. If some difference persists, I would expect both chemically crosslinked products to suffer from loss of gas at amide groups. (Nylons perform poorly.)]

The pyrrone polymers are made from condensation of dianhydrides and di-o-diamines and contain the functional grouping,



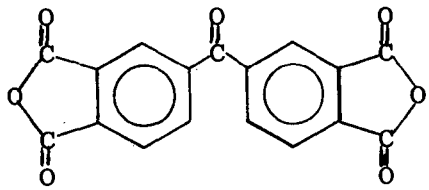
The name is derived from polyimdazopyrrolone and was proposed by the group at Langley Research Center that developed them. The principal representative of the group in papers from Wright-Patterson Air Force Base and its contractors is made from 1,4,5,8-naphthalenetetracarboxylic acid dianhydride and 3,3'-diaminobenzidine, has the class name polybenzimidazolone, and is designated BBB. It has a biphenyl link from the benzidine. The polymer from 1,2,4,5-tetraaminobenzene, with a full ladder structure, is designated BBL.

Bell and Jewell[15] describe the syntheses and some properties of eight pyrrones from two dianhydrides and four tetramines:



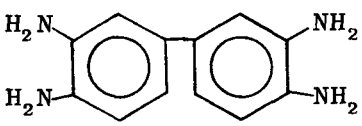
Pyromellitic dianhydride

PMDA



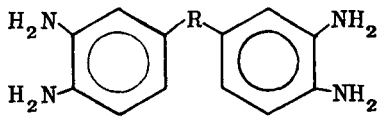
3,3′4,4′-benzophenone tetracarboxylic dianhydride

BTDA



3,3′-diaminobenzidine

DAB

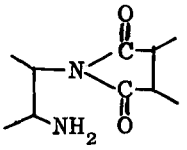


R=-C(=O)- 3,3′,4,4′-tetraaminobenzophenone TABP

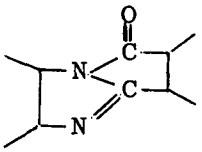
R=-CH(H)- 3,3′,4,4′-tetraaminodiphenylmethane TADPM

R=-O- 3,3′,4,4′-tetraaminodiphenyl ether TADPO

Most of the polymers were made by slow addition of the anhydride to the amine in a solvent such as N-dimethylacetamide or N-dimethylformamide near room temperature, but alternative methods used amine hydrochlorides, esters, or acid chlorides. The low-temperature condensation appears to give mostly the amine-polyimide,



which cyclizes to the pyrrone,



on heating. The polymers were soluble and colored, with number-average molecular weights up to 15,000. Cast films cured 3 hours at 250° (in air, nitrogen, or vacuum) had tensile strengths of 1000 to 2200 psi, high moduli, and only 2 to 4% elongation at break. The PMDA-DAB polymer (BBB) maintained 70% of its room-temperature tensile strength at 200°. Somewhat higher tensiles and moduli were obtained from 300° cures. The polymers were unusually stable to ionizing radiation and to concentrated acids and bases.

Thermal stabilities of these polymers are discussed in two papers, one where four films were compared,[16] and a later one where all eight were compared.[17] Films were cast from solution on glass, dried, and cured for one hour at 125°, and then cured further for 2 hours at 350°[16] or 300 300°[17] in air. Every film was then preconditioned for pyrolysis by heating to 100° for 30 minutes to remove water. The first paper is of interest in showing the limitations of TGA.[16] Here, TGA were made on BTDA-DAB at constant temperatures of 440°, 450°, and 460° in air. At each temperature

there was a rapid weight loss after an initial induction period decreasing from 150 to 80 minutes. In ordinary TGA, rapid weight loss was delayed to 500° to 600°. [These data establish that there is an important auto-catalytic oxidation of at least this pyrrone and that initiation reactions at moderate temperatures are wholly missed in TGA.]

TGA were run on the eight pyrrones both in air and in vacuum.[17] The two sets of results start to diverge at 300°. In air, rapid and nearly complete weight loss occurs near 500°; in vacuum, the fastest weight loss occurs near 550°, but the ultimate weight loss at 800° is only 25 to 35%. Differences among the polymers are small; polymers from BTDA may be slightly more stable than those from PMDA. With either anhydride, the polymer from TABP was most stable, that from PADPO lease stable, but differences were small. Jewell[17] concludes that the stabilities of the polymers increase with their [theoretical] carbonyl contents. [I suggest a modified explanation: In comparison with other connecting links between benzene rings, the benzophenone carbonyl provides protection against oxidation below 500° but none against pyrolysis above 600°.]

Changes in infrared absorption during heating at constant temperature suggest that imide formation is strongly developed in 1 hour in air at 300° but 400° in vacuum was required for formation of pyrrone structure, still without complete loss of imide groups. [Comparison of these results with the TGA results above again indicates the very limited usefulness of TGA, either for detecting changes in structure or for measuring decomposition temperatures.]

Each polymer exhibited three different regions of weight loss when heated in vacuum. In the region centered at 390°, water was the principal gaseous product, accompanied by development of the imidazole (-C=N-)

band. In the 500° to 600° region, CO was the principal gas, with small amounts of CO_2, H_2O, and NH_3, accompanied by gradual disappearance of imide and pyrrolone carbonyl groups but retention of benzimidazole groups. [The higher yields of CO from the polymers with benzophenone units suggest that this unit adds no extra stability above 500°.] The third region of weight loss near 720° produced mostly HCN. Above 800° in vacuum, the char tends to stabilize after 25 to 35% weight loss, greatest when most CO is available for loss.

[Several considerations suggest that the pyrrone polymers do not have regular structures and that they contain fewer pyrrone groupings than they are supposed to have.] First is the loss of water at 400° and development of pyrrone, noted first above. Further, any excess or solid anhydride during their preparation causes gelation. The last portion of the theoretical anhydride was added slowly at room temperature. [Solubility does not prove the absence of crosslinking; with silicones I have obtained highly crosslinked but still soluble polymers.[18]] Attempts to make polymers of intrinsic viscosities above 2 led to gelation. That the BBB polymer had as high a modulus at 200° as at room temperature suggests further crosslinking on heating. [These results are consistent with a condensation and a cure that give mostly, but not entirely, the supposed pyrrone structure. Thermodynamically, the possibility of making a perfectly regular polymer from two tetrafunctional monomers seems remote. A pair of amines should occasionally react with one carboxy group to give an imidazole, or a pair of carboxyls with one amine group to give an imide. The unreacted groups of the pairs may then give similar products, amides, or amine salts.] The polymers absorbed 5-7 wt% of water,[16] 1 to 2 moles per formula weight, at room temperature and lost it perfectly reversibly at 100°.

Van Deusen and coworkers[19] prepared pyrrone polymers from 1,4,5,8-napthalenetetracarboxylic acid dianhydride with 3,3'-diaminobenzidine (to give BBB) or with 1,2,4,5-tetraaminobenzene (to give BBL) in polyphosphoric acid. The condensation to BBB was closer to completion and gave a polymer that was more soluble in concentrated sulfuric acid. The black polymers were also soluble in concentrated aqueous alkali, from which they could be recovered unchanged. By TGA BBB showed no weight loss to 600° in nitrogen; BBL lost 2 to 4% under these conditions. Weight losses in air began at 450°.

Gaudiana and Conley reported the pyrolysis of a purified sample of BBB supplied by the Materials Laboratory of Wright Patterson Air Force Base. It behaved much like the corresponding sample of PBI. [Comparison of the TGA data on Conley[20] and of Jewell[17] is unrewarding; the 150°/hr heating rate of Conley gives a rapid decomposition in air near 600°, compared with 500° at the 1°/min heating rate for the polymers of Jewell.] However, comparison of Conley's DTA (not TGA) data in air and nitrogen indicates that oxidation of BBB begins at 270°.[20] [This result reveals again the weakness of TGA.]

When BBB was heated in a stream of oxygen at 500° for product analysis,[13,21] the principal gases were $CO_2 > CO >> (CN)_2$. The only readily condensible product identified was water.

Goldfarb and Bain[22] pyrolyzed BBB by TGA in vacuum at different heating rates from 75° to 450°/hour and analyzed the results by computer. The total weight loss to 1000° was 20 to 23%, depending on the rate of heating. Analysis of the results by computer indicated an apparent activation energy of 85 kcal/mole at 10 to 80% reaction and an apparent reaction order for weight loss of 1.7. [Although their numbers describe their results very well, except at the beginning of pyrolysis, they must apply to a composite of several unresolved reactions.]

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MODELS FOR POLYBENZIMIDAZOLES AND PYRRONES

Gaudiana and Conley also present data on thermal degradations of PBI and BBB for comparison with three pyrrone models (I to III in Figure 1) and four polybenzimidazole models (IV to VII).[12,20,21] I take up first two series of experiments where samples were heated in oxygen or helium for 30 minutes at several constant temperatures and the residues were then analyzed. In one series, compounds I to VI were heated at a series of temperatures from 250° to 600°. Here more details appear in Refs. 13 and 23 than in 20. In oxygen at 250°, weight losses in 30 minutes were 0 to 1%. At 300°, losses were 1 to 1.4%, except that VI lost 6.7%. At 350°, the spread among samples increased from 1.15% for VII to 8.0% for VI. For models II and III, pyrolyses were run in helium as well as in oxygen at 250° to 350°.[23] Although slightly less weight is lost under helium, the differences seem to be of the same magnitude as the experimental error. For Model I, tests were extended to 600°.[20] Weight loss in 30 minutes reached about 13% at 450°, in either oxygen or helium. However, at 600°, the weight loss was 97% in oxygen. These data indicate that oxygen is not involved in the initial pyrolysis of at least some models at lower temperatures. [But more sensitive infrared or pretreatment experiments might yield a different conclusion. Of most interest would be longer experiments at 250° to 300°, to see whether autocatalysis of oxidation sets in].

In a second series of experiments, Models I to VII were heated in oxygen for 30 minutes at 450°, and the elementary analyses of the residues at that time are given[20] [However, the basis for calculating the results is confused (residue V appears to contain 57% oxygen!), and so the conclusions may have only limited significance. The conclusions on Model VI in this and the above paragraph are inconsistent.]

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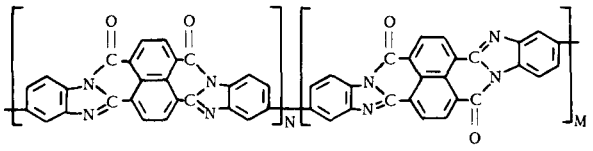
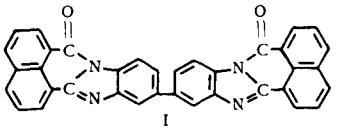


PYRRONE (BBB)



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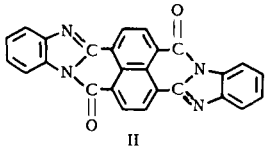

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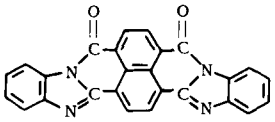

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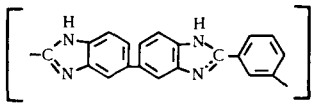
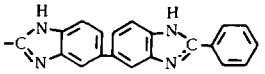
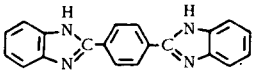


POLYBENZIMIDAZOLE (PBI)



IV



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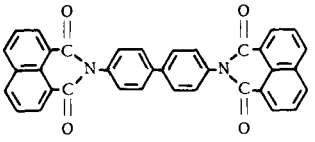
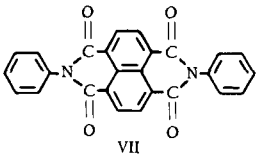


VI



VII

TA-1324-1

FIGURE 1 POLYMERS AND MODELS STUDIED BY GAUDIANA AND CONLEY [12, 20, 21]

"The chars obtained from those model compounds which contained amine residues as end groups (II, III, V, and VII, Fig. 1) revealed large depletions in percent carbon, hydrogen, and nitrogen; those models which had acid residues as end groups (I, IV, and VI, Fig. 1) revealed large losses in percent carbon" [but not as large as with other groups] "while the nitrogen content either decreased by a relatively minor amount or increased."

Differential thermal analyses (DTA) were run on a few samples at a heating rate of 20°/min.[20] [Comparison of results in air and nitrogen indicate that oxidation of BBB began at 270° and of Models I, II, and III at 310° (below its melting point, 449°), 380°, and 430°, respectively.]

References 12 and 21 describe pyrolyses in a stream of oxygen at 500° of models and the two polymers in Figure 1, with occasional data at other temperatures or in helium. Qualitative analyses were made on the gases, the sublimates, and the residues. Apparently the gases were sampled at 5 or 10-minute intervals during the early stages of the oxidations, mostly by infrared absorption, but no weight changes are indicated, even for the final chars.

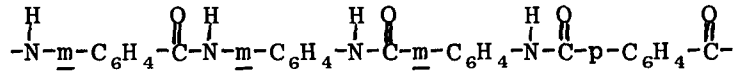
The gases are mostly CO_2 and CO with a little cyanogen. Water was also found but nitrogen and nitrogen oxides were not. [However, nitrogen must have been evolved as the char oxidized.] The only other products carried over and identified (except some starting models as sublimates) were acid anhydrides or nitriles corresponding to the acids from which the compounds were made. In spite of careful search, no products were found with nitrogen attached directly to an aromatic ring. It is concluded that pyrolysis and oxidation begin at the heterocyclic rings or at the aromatic rings attached to nitrogen, with subsequent rapid disintegration of these rings. In general, the infrared bands in the samples gradually weaken and broaden with conversion,[12,21] and the ratios of CO_2/CO increase with increasing extents of oxidation.[20]

Pyrolyses of Model IV were compared qualitatively at several temperatures and in oxygen, air, nitrogen, or helium.[21] In oxygen, temperature change had little qualitative effect. In an inert atmosphere, changes in infrared absorption are qualitatively the same as in oxygen.

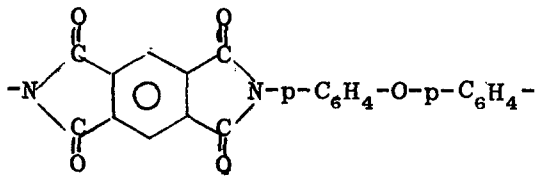
A recent Conley paper[25] describes the incorporation of 20 weight % of Models IV, V, a longer one with features of both, and Model IV with two p-carboxy or two p-amino groups in the terminal rings into films of PBI. The formation of nitrile infrared bands was then followed during 5 hours of oxidation at 300°. The results show that rings with free carboxyl and amino groups contribute to nitrile formation but that the other models do not. These results suggest that end groups and incomplete condensations in PBI contribute to its instability.

PYROLYSES OF AROMATIC POLYAMIDES AND POLYIMIDES

Ehlers et al.[26] investigated carefully the pyrolyses in vacuum of one polyamide and four polyimides. The results are included here for comparison with the benzimidazoles. The polyamide had the repeating unit,



The simplest and representative imide had the repeating unit,



As measured by either the total weight loss or the temperature at which it is lost, the amide is least stable, the benzimidazole is most stable, and the imides are intermediate. One vacuum pyrolysis, the amide lost 26.5% of its original weight up to 375°, 22.5% more up to 450°, nearly two-thirds as "sublimate." The gases were mostly CO_2, with about half as much CO. Nearly all the oxygen has been lost from the residue at 450°, but the %N has decreased only slightly. The four polyimides behave much alike. The indicated one lost only 3.4% of its weight up to 400°, mostly as CO_2. Up to 350°, 27.5% more was lost, two thirds as CO and CO_2. Relatively little "sublimate" was formed. At 550°, most of the oxygen had been lost from the residue but the %N was little changed. Closely comparable data for PBI are not available, but 400° is required to bring the condensation to a reasonable stage of completion.[6] Further heating to 800° in an inert gas then results in only a 15% weight loss (85% yield of char).

The most remarkable feature of the decompositions of the amides and imides is the large and relatively easy loss of CO_2, although no carbon atom in the polymer is supposed to be attached to more than one oxygen atom. The most interesting explanation[26] is that isocyanates are intermediates and that they react,

$$2ArN{=}C{=}O \rightarrow Ar{-}N{=}C{=}N{-}Ar + CO_2$$

[Although free radical mechanisms are proposed for formation of isocyanates, these require scission of aryl-carbon bonds, and cyclic mechanisms should require less activation energy. Tests on model compounds might be useful.]

With the amide, most of the weight is lost as high-boiling products. [Pyrolysis at higher pressure might avoid part of this loss. Perhaps the amide hydrogen is responsible, and its replacement by methyl might result in stabilization to the imide level.]

With either amide or imide, most of the rest of the original oxygen is evolved as CO_2 and CO. Apparently nitrogen and sulfur are incorporated into the char but oxygen is not. [Thioamides and thioimides, by incorporation of S into the residue, might give more residues and less gas evolution.]

CONCLUSIONS

[There are two main questions in understanding the pyrolysis of heterocyclic polymers. How and where does the breakdown of these polymers begin? What goes on during the final charring process? Unfortunately, most of the data reviewed above were obtained in an intermediate temperature range, where several kinds of reactions are going on together, and provide little information on either question. Most of the data are TGA, a most unsatisfactory probe, as pointed out repeatedly in the sections above. The popularity of the intermediate temperature range and of TGA are apparently due to their convenience; publishable but not very useful data can be obtained rapidly.]

[The meagre information on the high-temperature reaction is considered first. The work on polyphenylenes demonstrates the cross-linking and condensation of polyphenylene chains by dehydrogenation. The evolution of methane and the formation of condensed aromatic structures indicate that considerable reorganization of benzene rings must occur. Although on paper it is possible to convert a sheet of perfectly aligned p-polyphenylene molecules to a sheet of graphite by loss of hydrogen without rearrangement of benzene rings, this ideal situation will be nearly impossible to approach in practice. However, with sufficient time and the right environment, incipient graphite structures probably evolve into more advanced ones.]

The heterocyclic polymers lose all their oxygen as carbon oxides on sufficient heating in an inert atmosphere. Some heterocyclic nitrogen is retained, [but I cannot tell whether this nitrogen is desirable for assisting rearrangements of aromatic rings or improving performance of the chars. In view of the rearrangements that must occur

on charring, the distinction between thermal and chemical crosslinking seems unjustified.]

The rest of this section will present some generalities from the intermediate temperature range and the best clues that are available about the onset of pyrolysis, with and without oxygen. The order of stabilities of aromatic nitrogen-containing polymers is amides < imides < pyrrones < imidazoles. The extensive and relatively easy loss of CO_2 from amides and imides, when they contain only $C-\overset{O}{\overset{\|}{C}}-N$ groups is ascribed by Ehlers et al.[26] to the formation and decomposition of aryl isocyanates and may be an important clue to decompositions of other nitrogen heterocycles.

All the heterocyclic polymers leave substantial proportions of char when heated to 800° in vacuum. Essentially all of them disappear when heated slowly to or at 500° in air. Char, sometimes in substantial proportions, can be obtained temporily by rapid enough heating in air,[6] but it will subsequently disappear.

There are statements that oxygen does, and does not, affect the initial decomposition of heteroxyclic polymers. [The former are more convincing.] Conley's infrared work on purified PBI suggests that decomposition starts in vacuum at 500° but becomes significant in oxygen at 300°. However, his weight loss studies indicate 9% weight loss in 30 minutes at 300° when infrared finds little change. Another of his reports indicates that preheating a film to 450° in helium, where no decomposition is supposed to occur, slightly accelerates subsequent oxidation at 300°. However, his work on models shows no surely significant effect of oxygen at 250° to 350°. [These results suggest that a single adequate criterion for stability and initial decomposition has not yet been found, and that some criterion is badly needed; it may not be a simple one.]

Fewer data are available on pyrolysis of the pyrrones. The infrared data demonstrate that the last step in the condensation (closing of fused ring) is slow, difficult, and ordinarily incomplete before other pyrolysis reactions set in. The reported work on pyrrones offers two very interesting leads. When films of BTDA-DAB were heated at 440°, 450°, or 460° in air, there was a rapid weight loss after an initial induction period decreasing from 150 to 80 minutes (shortest at highest temperatures). [These results establish for this polymer an important autocatalytic oxidation process of unknown generality.] DTA (not TGA) indicates that oxidation of BBB begins at 270° in air, a surprisingly low temperature.

[The work of Gaudiana and Conley on PBI, BBB, and models of these makes some important points and misses some others]. First, the models are heavy enough molecules that volatility is not a problem. Second, they are good models for ideal portions of the polymers. Since they can be recrystallized and sublimed, they are "purer" than any heterocyclic polymer is likely to be, and slightly more stable. Third, the data indicate conclusively that model end groups that were originally diamines are oxidized and lost more rapidly than the acid end groups. Fourth, the data suggest that free amino or carboyxl groups at the ends of the normal polymer molecules contribute to instability. Fifth, heating of Model I in oxygen for 2-1/4 hours at 300° caused flashing, not otherwise observed during the first hour at heating at 400°. [This result seems to be a neglected opportunity to study the effects of pretreatment.]

DTA indicate that oxidation begins at 270° to 310°, depending on the model, often below the melting point of the model. Unfortunately, most of the oxidation data were obtained by heating samples in a stream of oxygen for 30 minutes at 500°, where most of the materials burned away. Flashing and glowing are mentioned for some samples; [these raise doubts about the other samples and show that the reaction conditions

were too strenuous.] The off-gases were mostly CO_2, with less CO and still less cyanogen. Very small amounts of acid anhydrides and nitriles were obtained but no evidence of aromatic amines.

SUGGESTIONS FOR FURTHER WORK

Objectives

The objectives of the work proposed below are to determine the mechanisms of the initial breakdown of conjugated aromatic polymers (with the hope of improving maintenance of their original physical properties), and to obtain chars (on pyrolysis in inert atmospheres) with improved ablation properties or at lower costs. The more important suggestions are marked*.

Criteria of Stability

[I propose that weight change during long heating at a constant temperature 250° to 350° in a stream of air be used as the primary criterion of stability.* The test must allow for prior removal in vacuum, or loss during test, of condensation products. Secondary criteria of stability are changes in IR absorption and physical properties of films of molded specimens. I think that the wide use of TGA has overestimated the stabilities of the most popular polymers.]

Involvement of Oxygen

There are claims that oxygen does and does not affect the onset of pyrolyses at the lowest temperatures. [Some representative polymers should be tested by the criteria above in long-term tests, at the lowest practial temperature, in oxygen and in inert gas.* If differences are found, the effects of oxygen pressure should be determined to see whether oxygen participates in a rate-determining step. Is the single reported autocatalytic oxidation general?* Does preheating a polymer in vacuum at the highest temperature where it appears to be stable by the criterion above affect its subsequent oxidation?]

Effects of Other Variables

[A major unknown factor in the stabilities of aromatic polymers is the degree of condensation and the effects of ash and other impurities. Comparison of polymers at various high degrees of condensation with models that can be sublimed may provide the best answer to this question.* Complete or equilibrium condensation probably requires a solvent and a condensation catalyst. Polyphosphoric acid may serve as both, but a milder combination, such as a solvent (e.g., phenanthrene or carbazole) plus an optimum concentration of a catalyst (e.g., naphthalene sulfonic acid) should be tested. A refluxing solvent will assist removal of lower-boiling condensation products. Condensations are probably less complete than commonly supposed. A test for degree of condensation is desirable.]

Criteria of Mechanism

[Electron spin resonance measurements should be made on a conjugated polymer, as prepared and purified, and during its pyrolysis in air and an inert atmosphere. I expect to find some signal at all stages. Are changes in esr signals a useful criterion of stability and mechanism?]

[If the polymers contain or generate interesting concentrations of radicals, these might be reduced and labeled by reaction of the polymer with deuterated mercaptans, hydrogen sulfide, hydrogen bromide, or deuterium itself.* If radical sites cannot be thus determined, total radical formation might be measured by absorption of tritium from a suitable source. If there is any chain character to a free radical decomposition, the reaction should be slowed by a source of active hydrogen such as propylene or toluene.*]

The suggestion that polyamides and polyimides decompose via isocyanate groups is an interesting one because polybenzimidiazoles and

pyrrones probably contain appreciable proportions of such groups. [The suggestion should be tested with models of polyamides and polyimides. If isocyanates are involved, they should be added to pyrolyzing benzimidazoles and pyrrones to determine their effects on those decompositions.]

Reservations

[The following possibilities should be considered in planning further work on the mechanisms of decomposition of heterocyclic polymers. No compound containing carbon and hydrogen will indefinitely withstand exposure to air at 300°C. Yields of 100% of the desired polymers are impossible with monomers with three or four functional groups. The stabilities of the condensation products may depend more on unreacted functional groups and by-products than on the structures of the intended ideal polymers. Thus, further work may prove unrewarding. However, several of the experiments proposed above are intended to assay these possibilities.]

Char Formation

[Although one report suggested that much of the hydrogen might be lost from polyphenylene as methane, there is little indication that this route is important with poly(chlorophenylene)s or heterocyclic polymers. Since the formation of methane must be associated with reorganization of aromatic nuclei and is thermodynamically favored below 520°, catalysts and retarders for this reorganization route should be sought.* Candidates are iron, nickel, cobalt, chromium, their oxides, ash constituents, and boranes. Do polymers containing heteroxyclic nitrogen or sulfur rearrange more easily than those that do not?]

Carrying out Pyrolyses

[Some gases might assist the reorganization process or supply carbon to increase char yields or densities: CO, methane, ethylene, acetylene, propylene, butadiene.*]

[This question is important: after the same high-temperature cure, and at the same char density, does the nature of the aromatic polymer that became the char make much difference?* If it does not, then we should consider cheaper alternative sources of carbon. If this approach proves to be unpromising, then research is in order to find out why the source of the carbon is important.]

[The direct synthesis of chlorinated polyphenylenes from benzene gave only 50 to 60% of polymer precipitated by methanol. The soluble material probably contains chlorinated benzenes, biphenyls, and terphenyls that may be nearly as good as the insoluble material for ultimate conversion to a polymer approaching graphite. They should at least be recycled. If our objective is to approach formed graphite economically, we might simply heat trichlorobenzenes under pressure conditions such that the HCl gas would escape but the organic material would not.* (This condensation could be explosive.) Another approach is to start with oxidative chlorination of, or chlorinated, polynuclear hydrocarbons such as naphthalene, anthracene, phenanthrene (the cheapest), or even pitch, reducing the resulting reorganization and shrinkage.]

Mr. Bernard H. Achammer has suggested that the applications of reorganization of aromatic nuclei may be more important in carbon fibers than in ablation shields or brake blocks.

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APPENDIX

Reference 2 in attached report

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CERTAIN SPECIAL FEATURES OF DEGRADATION OF POLYMERS WITH A CONJUGATION SYSTEM

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In the last few years the demand in polymer materials with long working period at high temperatures has greatly increased. A number of recently synthesized polymers with a conjugation system (PCS) /1/ in many ways meets these requirements. However, the task to increase thermal stability of polymer materials is seriously complicated since at present the unique, generally accepted, theory of the effect produced by special features of chemical structure of polymers on their thermal stability is absent. It is also known that due to different conditions in which the tests are performed, methods and equipment used in research, as presented in printed data, it is not always possible to compare thermal stability of polymers, which differ by their chemical structure. Trying to find the correlation existing between the special features of PCS structure and their thermal stability we studied in one and the same experimental conditions the stability of certain classes of PCS. Polymers stability in vacuum, inert gas and in air has been studied. The value of decomposition was estimated using the weight loss of polymers when they were heated with a constant rate or in isothermal conditions. Loss of weight was recorded automatically on electronic thermal weighing machine /2/.

Changes in chemical structure of polymer during degradation were estimated by data supplied by IR- and EPR-spectroscopy, x-ray structural and differential-thermal analyses as well as by microanalytical method of determining elemental composition. By studying PCS stability the following polymers were taken as an example: polyarylens (polymers based on benzene, naphthalene, anthracene) /3/, polyarylvinylenes

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(polymers of phenyl- and pyridyl-acetnylenes) /4/, polyheteroarylens (polyaroylene-bis-benzimidazoles and polyarylene--bis-bensimides) /5/, polyazoarylens (polymers based on benzidine and certain phenols) /6/, polymers and polymer complexes with metals, synthesized from tetracyanethylene and tetracyanbenzene /7/, as well as a number of polymer quinones /8/. The weight loss curves of some reseached PCS are shown in Fig.1-3.

The obtained experimental data on PCS thermal stability result in certain conclusions about special features of their degradation. The specific character of this process is shown, first of all, in the form of the weight loss curves. By heating PCS in the absence of oxygen high degradation rates are usually observed at first, and afterwards the polymer does not loose the weight any more. This phenomenon to be conventionally called - the autoinhibition. If temperature during the testing is gradually rising the weight loss curve has usually the shape as shown schematically in Fig.1-a,b and as an example we may take polymer of 2-methyl-5-ethinylpyridine (PEP) and its block-copolymer with p-diethinylbenzene /Fig.1-c/. The curves similar to those shown in Fig.1a are obtained on degradation of polymers, having the aromatic conjugated fragments in the main chain as, for instance, polyarylens, synthesized by the method of cation dehydropolycondensation /9/. The second type of the curves is characteristic for the less thermally stable polymers, such as - polyphenylacethylene (PPA) /10,11/, as well as of certain saturated polymers, such as - polyvinylchloride /12/. As it is known the latter being thermoheated will have the aromatic conjugated fragments.

The study of elemental composition of polymer residue after degradation indicates to the processes of carbonization taking place, that is - carbon enriching of the products and increase in the extent of aromatic structure.

On those processes it is usually observed that intensity of characteristic absorption bands in IR-spectra of the thermo-heated products was decreased, intensity of EPR signal was increased up to a certain limit, solubility dropped, softening point became higher and colouring deeper. These facts produce the evidence that the phenomenon of autoinhibition is connected not only with the consumption of weak bonds in polymer, but is determined by a principal reconstruction of original structure. Mechanism of PCS degradation in most general meaning of that conception, can be apparently described as follows.

At the initial stage of PCS degradation the radicals are formed which are the products of the thermal cracking of the weak bonds. Such can be the structures unformed on the synthesis as well as fragments of polymer chain where, for one reason or another, the conjugation is cut off, for instance, as a result of taking out of caplanarity or due to the presence of chemical groups disturbing delocalization of unpaired electrons along the chain. Re-combination of radicals, formed at breaking of the chemical bonds, brings about the production of the substances with more increased conjugation system. Further degradation transformations will probably come to dehydration and increase in the extent of the structural aroma. Most probably, the carbonized polymer residues are themselves by a system of aromatic or heterocyclic condensed rings. It is supposed that in the end they should transform into the graphite-like structure, but the mechanism of that process is not yet known. As it has been mentioned above the carbon enriched polymer residues are the products with more increased conjugation system when compared with the original structure. Since this process is followed by decrease in internal energy of the whole system, as a result of the increasing of the conjugation chain, it is justified energetically. The conclusions are the following:

firstly - the thermal stability of PCS, in our opinion, mainly connected with possible transformation of original structures on heated into more energetically efficient ones;

secondly - since the ability to form such structures is characteristic of PCS of different chemical formation, the determining factor of thermalstability, in this case, cannot be the energy value of dissociation of bonds in macromolecula, as suggested in /13/.

Actually, the experimental data indicate to the fact that PCS, characterized by various strength of bonds in the main chain, such as p-polyphenylene (PP), polynaphtoylene--bis-benzimidasol (PNB), polymer complex of tetracyanethylene with copper (PTCE) and others, when heated in vacuum up to 800°C, form an equal number of polymer residues, what indicates their thermalstabilities being close to each other /Fig.2-a/. In support of this conclusion the printed data presents the results of work on synthesis and study of the properties of polyheteroarylens /14-17/.

It is shown /14,15/ thermalstability of many polyheteroarylens comperatively little depends on structure of the repeating unit, molecular weight, softening point and degree of crystallinity. The degradation mechanisms of these polymers are also very close to each other. In particular, the initiating of degradation usually consists of the breaking chemical bonds in heterocycle /16,17/. Further to that process various cross-linking reactions are added.

These facts bring about the conclusion that higher thermalstability of polyheteroarylens is not bound with special strength of heterocycle bonds. Evidently, it is explained by higher thermodynamic stability of the whole system as it is known that heteroatoms, present in heterocycle, do not disturb delocalization of the unpaired electrons along conjugation chain. Similar characteristic features of thermal transformations for PCS of different structure

and for certain saturated polymers, such as polyvinylchloride /12/, polyacrylonitrile /18/, and others, which could be transferred into PCS when heated, makes it possible to consider the specific process of degradation of these polymers as being due to peculiarities of the structure of polyconjugated fragments. According to modern opinion /19/ PCS is a set of macromolecules which differ by molecular weight and extent of conjugation block. Diamagnetic and paramagnetic polymer homologs with different length of conjugation chain form between themselves π-complexes, what increase reaction ability of the whole system. Because of that, PCS can perform the chemical transformations, not characteristic for the saturated polymers, for instance - reactions of block-copolymerization. As it has been recently shown /20/, the main diamagnetic portion of macromolecules, participating in chemical reactions, is activated in that process by paramagnetic component. Apparently, to the same type of reactions we can refer the process of degradation polymerization which takes place when PCS are heated. This makes improbable the progressing degradation of polymers at the partial breaking of the chemical bonds in macromolecules.

When studying thermal oxidative stability of PCS we found out the following.

It is shown that in this case the phenomenon of autoinhibition is most vividly indicated in degradation of those macromolecules in which the structural transformations are possible. Polymers in which the processes of aromatization and chemical cross-linking took place at the stage of formation or block-copolymerization have no the autoinhibition. It is seen when the curves of weight loss of PEP and its block-copolymer with p-diethinylebenzene are compared /Fig.1-c/. The fact that the processes of autoinhibition are characteristic of PCS especially is confirmed by comparing PPA weight loss curves with those of low-molecular polystyrol

/Fig.3-a/.

In the case of polystyrol, which is an analogue to PPA by structure but differs from it by absence of polyconjugation fragments, the process of autoinhibition does not take place. On heated PPA in air, contrary to thermal transformations in the absence of oxygen, after the autoinhibition the weight losses begin to show again /Fig.3-a/. The form of the weight loss curves as well as the data on determination of elemental composition of PPA indicate to indentical nature of chemical transformations at initial stage of degradation of the polymer in air and without air (see Fig.1-c and 3-a). It confirms that at the initial stage the thermooxidative degradation is close to thermal. In this case, as well as on heated without air, the aromatic structures are formed. Thus, the oxidation itself, that is - the process making polymers transform into volatile fragments as a result of interaction with air oxygen, proceeds already on the products of transformation of initial macromolecules.

The study of thermal oxidative stability showed that PCS, prior thermal treated without air (or in air), in conditions in which no weight loss takes place are less stable than initial polymers when compared. It is evident when weight loss curves of polynaphtoylene-bis-benzimidazol (PNB) are compared with those of PNB previously heated under vacuum at 350°C for 12 hours /Fig.2-b, curves 2,4). The same phenomenon was observed for other PCS too. In the process of such treatment the elemental composition of PNB does not change but its solubility in conc. H_2SO_4 becomes lesser. Similar effect is observed when 1-3% of previously thermoheated product are added to PNB /5/. Such treatment does not affect on thermal stability of polymers in vacuum. The decrease in PCS thermal oxidative stability was also observed for the insoluble non-softening fractions when compared with the soluble softening fractions of one and the same polymer as

shown in Fig.2-b, anthracene polymer being taken as an example. It is interesting to note the contrary dependence was revealed when the same polymers were degraded in vacuum /3/.

When PCS oxidation takes place in isothermal conditions two types of the weight loss curves are obtained: usual curves without inductive period and autocatalytic ones. Acceleration of the process was observed on heated of those polymers, which degraded at high temperatures. This is characteristic for polyarylenes /3/, polyarylvinylenes /4/, and certain polyheteroarylens /5/ /Fig.3-c/.

It is known that autocatalysis on oxidation of the saturated polymers is the indication of the chain branched process.

Polymer peroxides and hydroperoxides are often as branching agents. As to PCS, another mechanism of this phenomenon should be assumed. Autocatalysis of PCS with participation of peroxides is hardly probable. The following facts give evidence to that effect: 1/ high decomposition points of polymers at which polymer peroxides are thermally unstable, 2/ absence of hydroperoxide and peroxide characteristic absorption bands in IR- spectra of polymers after thermal treatment, 3/ conservation of symmetrical EPR signal on heated of PCS (it is known that in the presence of peroxides the signal changes), 4/ acceleration of thermooxidative degradation of polymers by products which do not contain of peroxides, as indicated above.

It should be noted that in IR- spectra of polyarylens on their thermal treatment in air the characteristic absorption bands, referring to aromatic and polycyclic quinones were detected /3/. Naturally, the question was raised whether these quinones are the products of decomposition of polymer peroxides, responsible for the acceleration of thermooxidative degradation. If this suggestion is true it should be

expected that the intensity of carbonyl absorption has to grow along with the increase in the decomposition value of polymer. However, if we take p-polyphenylene as an example, it shows that with the rise in temperature of the test the characteristic absorption bands of carbonyl group completely disappear and the data on IR-spectra of the polymer confirm aromatic structure of the residue and the presence of double conjugated bond.

PCS, not containing aromatic rings in main or side chains, linear polyenes, for instance, obtained by dehydrochlorination of polyvinylchloride, easily react to oxygen /21/. The authors of this article assume that polyenes, when oxidized, evidently form cyclic polymer peroxides. Continuity of conjugation chain is disturbed as a result of this reaction. But it should be noted that heating of the oxidized polyene in air is not followed by progressing degradation, as it happens in case of usual polymer peroxides. Decomposition of the oxidized polyene in vacuum is also proceeded in another way. These facts confirm that PCS oxidation mechanism differs from oxidation of the saturated polymers. However, at present the process of interaction between PCS and oxygen are practically not investigated. Therefore, on the basis of the obtained experimental data it is impossible to come to any well-defined conclusion. Only hypothetical explanation of PCS oxidation mechanism can be given as under.

As it is known, the appearance of inductive period is connected with an inhibitor present in the system which is oxidized. The polyconjugated system itself acts as such. It contains complexing paramagnetic and diamagnetic polymer-homologs. Inhibiting activity of PCS is maintained till sufficiently stable donor-acceptor complex exists between the components. However, as a result of chemical reactions taking place on thermal treatment of polymers, the possibility of macromolecules complexing is diminishing, because the

products then loose their melting ability, and structural likeness between the complexing polymer-homologs is disturbed. Due to that donor activity of polyconjugated system is growing the interaction between the oxygen (acceptor of radicals) and the fragments of macromolecules with higher electronic density becomes possible. Besides, lower thermal oxidative stability of the thermoheated PCS, as compared with original polymers, as well as of cross-linked block--copolymers can be connected with the strainness and defectness of such rigid structures. Thus, PCS degradation is a complex process in which an important place is occupied not only by the reaction of breaking chemical bonds under heat (or oxygen) effect, but also by the cross-linking reaction between macromolecules and the products of their degradation.

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Inscriptions for drawings

Fig.1. Typical curves of weight loss of PCS on heated in the absence of air /a,b/
c. - for PEP /1,3/ and its block-copolymer with p-diethinylbenzene (2,4)
—— in air, –– in argon.

Fig.2. TGA of certain PCS in vacuum (a) and in air (b).
1 - PP, 2 - PNB, 3 - PTCE, 4 - insoluble anthracene polymer, 5 - soluble anthracene polymer, 6 - PNB, 7 - PNB, thermoheated under vacuum at 350°C
ΔT = 3°C/min (a), ΔT = 2°C/min (b).

Fig.3. Weight losses of PCS on heated in air:
a. PPA — -, polystyrol ——
b. PP ——, PNB ——

P-37

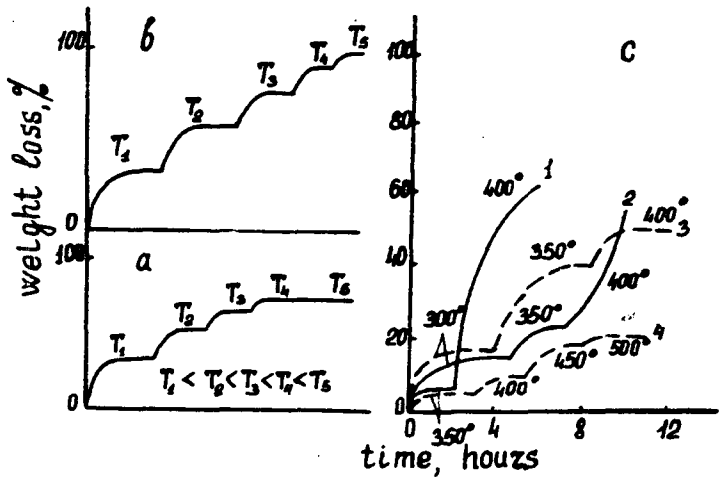

Fig.1

P-37

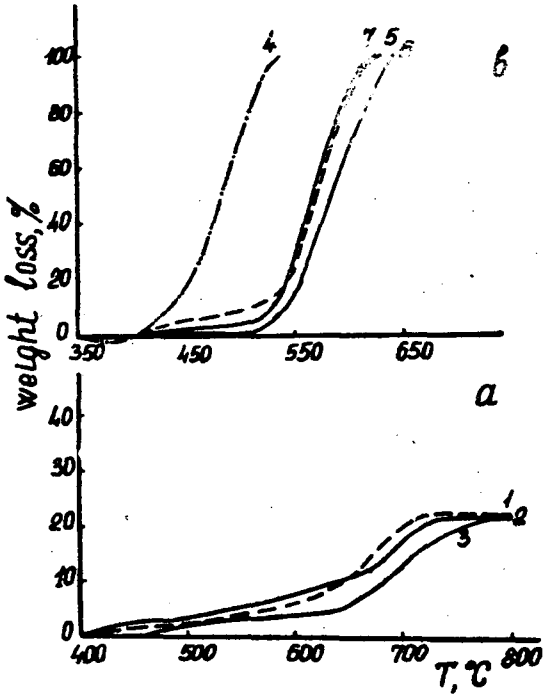

Fig. 2

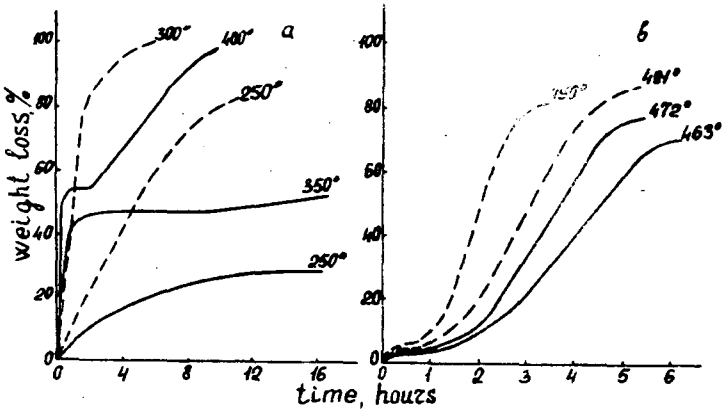

Fig. 3